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DESTRUCTION OF VOLATILE ORGANIC COMPOUNDS VIA CATALYTIC INCINERATION

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16. ABSTRACT The paper gives results of an investigation of the effect of catalytic incinerator design and operation on the destruction of specific volatile organic compounds (VOCs), both singly and in mixtures. A range of operating and design parameters were tested on a wide variety of compounds and compound mixtures. Conclusions of the study, presented here as applying only to the test catalyst and ranges of conditions tested, include: (1) VOC destruction efficiency increases with increasing temperature and concentration, and with decreasing space velocity; (2) the destructibility of VOCs varies according to compound class; (3) individual VOCs have different destruction efficiencies (at a given concentration, temperature, and space velocoty); and (4) different destruction efficiencies may be obtained for a specific VOC incinerated in a mixture vs. burned alone.

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Organic Compounds	Stationary Sources	07C
Volatility	Volatile Organic Compounds	20M
Incinerators		
Catalysis		07D

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INTRODUCTION

EPA's Air and Energy Engineering Research Laboratory conducts and sponsors research on technology to reduce or eliminate emissions of volatile organic compounds (VOC's) from industrial/commercial sources. Recently, a study on the use of catalytic oxidation to destroy VOC's (including potentially toxic air pollutants) was completed by Radian Corporation under an EPA contract. The study was designed to investigate the effect of catalytic incinerator design and operation on the destruction of specific VOC's, both singly and in mixtures. A range of operating and design parameters were tested on a wide variety of compounds and compound mixtures. This paper presents the results of this research effort.

BACKGROUND

Catalytic incinerators are used by a variety of industrial sources to reduce VOC emissions. Several catalyst formulations are sold for VOC control, although precious metal catalysts (e.g., platinum or palladium) predominate. Fixed bed systems with various geometries are available, as are fluidized bed units.

A recent EPA study summarizes the application of catalytic incineration in the US (1). While it has been estimated that over 500 catalytic units are operating in the US, the study identified only 149 specific facilities which employed catalytic systems for VOC control. These systems were distributed across the following industrial categories:

Solvent/Coating Application and Drying - 60%
Organic Chemical Production - 15%
Miscellaneous Processes - 25%

Field data were collected at eight incinerators in the Solvent/Coating industrial category. These data indicated that the design efficiency for VOC combustion was achieved at five of the installations. Two of the

incinerators had deactivated catalysts and achieved poor destruction. The remaining unit also showed low efficiency, but the space velocity was excessive.

EPA has also conducted tests of a pilot scale catalytic incinerator on the emissions from a flexographic printing press and a full scale unit on a formaldehyde plant (2). The pilot scale tests were conducted over a range of temperatures and space velocities. The results, shown in Figures 1 and 2, indicate that total VOC destruction efficiency exceeded 95% over the range of test conditions. The results also show that the destruction efficiency of specific compounds (e.g., propyl acetate and heptane) varied considerably from the total destruction under some conditions. Eight tests were conducted on the formaldehyde plant over a 10-month period. All the tests showed VOC destruction of 98% or higher.

PURPOSE OF THE STUDY

An evaluation of the literature on catalytic incineration (1) and the EPA testing previously conducted (see above) provides substantial information on the performance of catalytic systems. This information covers a multitude of catalyst materials and geometry, operating conditions, and VOC compounds and concentrations. Unfortunately, the information is insufficient to allow one to confidently predict the performance of a given catalytic incinerator applied to a specific VOC mixture. Only via ad hoc laboratory or pilot tests can such data be obtained.

The purpose of the study reported herein (3) was to conduct a comprehensive evaluation of catalytic incineration of VOC's to determine the effect of operating parameters (i.e., temperature and space velocity) and VOC waste stream characteristics (i.e., concentration, compound type, and mixture composition) on the destruction of specific organic compounds. The study was designed to identify the effects, not to determine their cause. It was hoped that the results of the study would assist in focussing future research on the most critical questions.

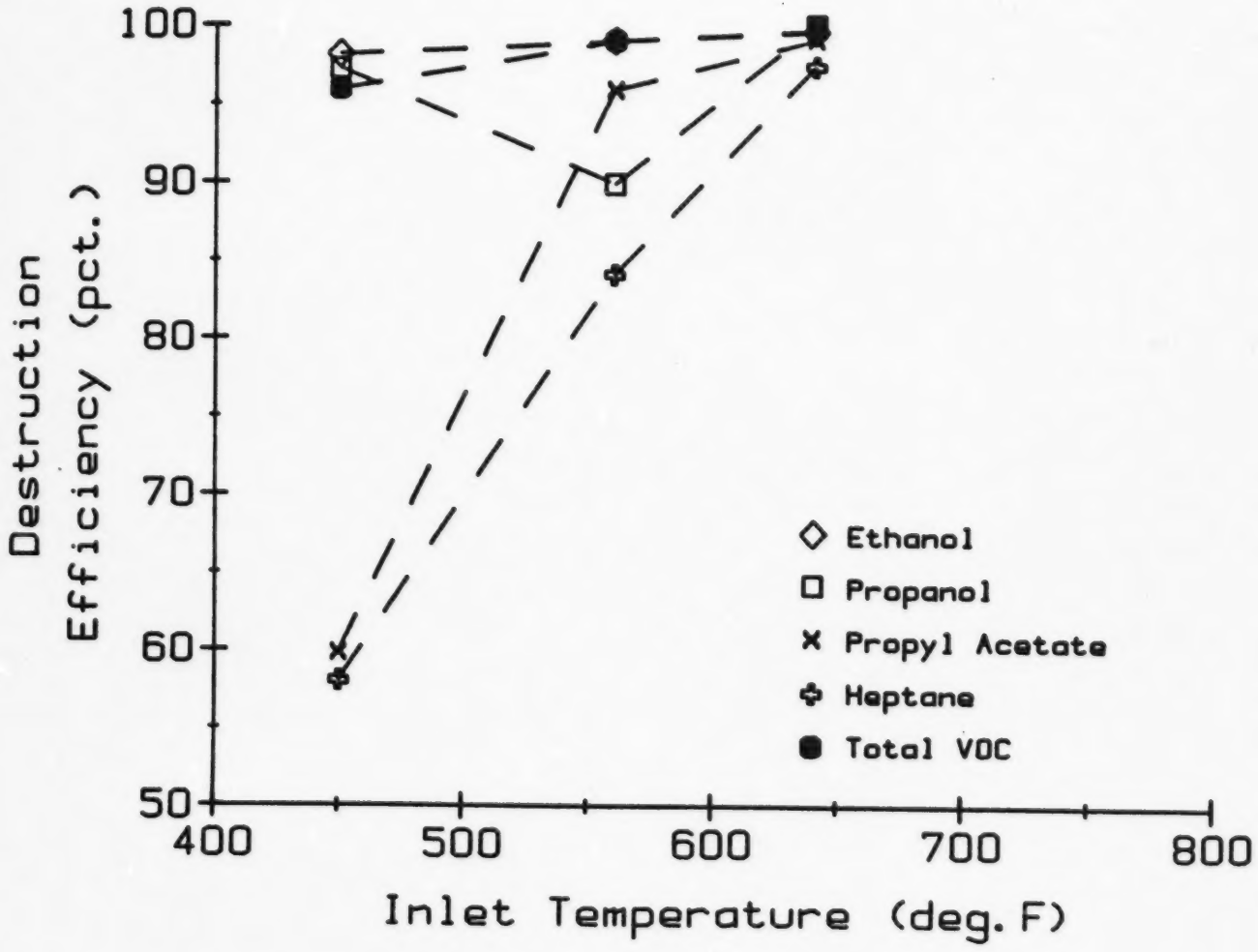

Figure 1. Destruction Efficiency for Flexographic Printing Emissions vs. Temperature (Space Velocity = 50,000/hr)

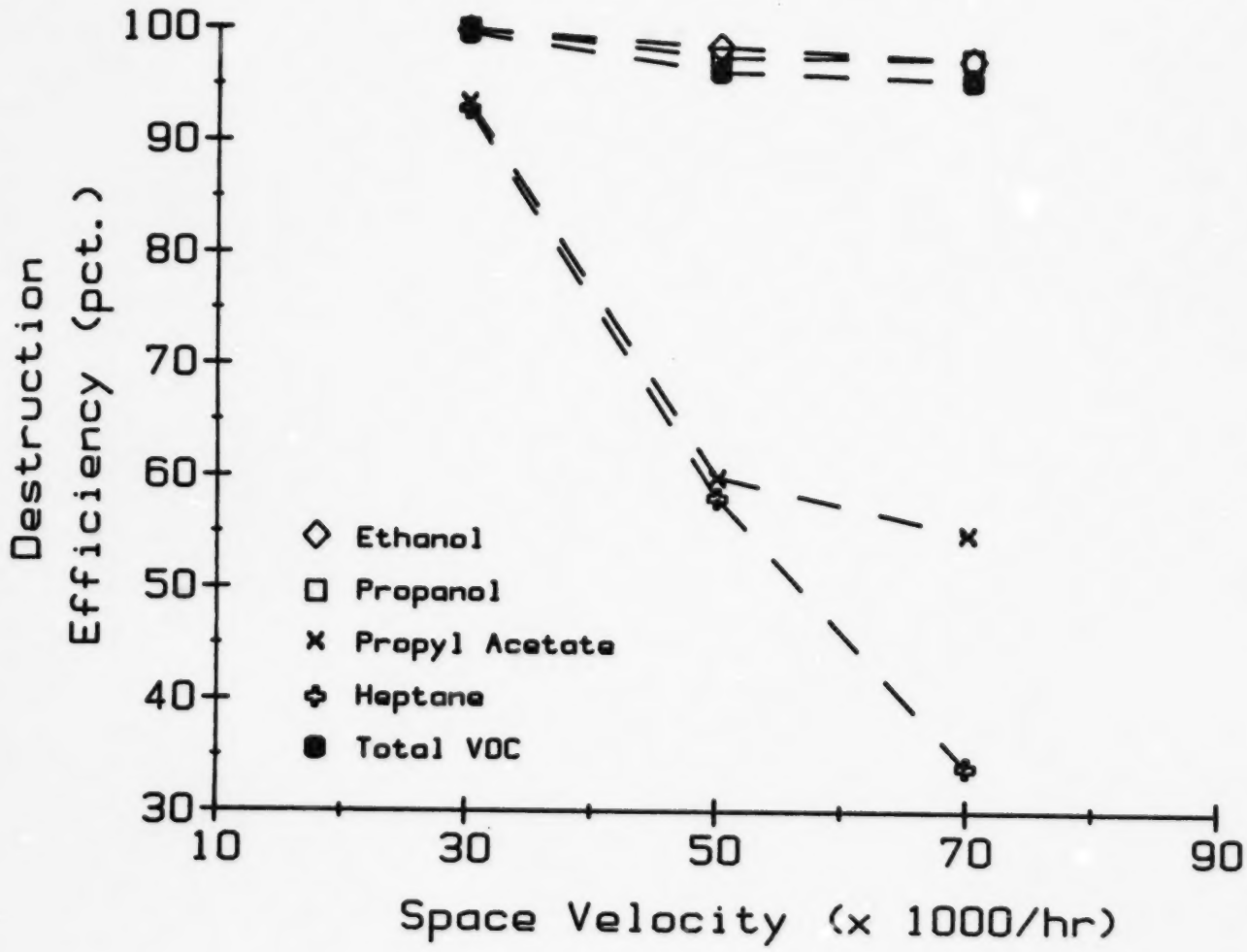

Figure 2. Destruction Efficiency for Flexographic Printing Emissions vs. Space Velocity (Temperature = 450 deg. F)

EXPERIMENTAL DESIGN

Test System and Methods

The test system consisted of a skid-mounted catalytic incineration unit and a solvent vapor generation system. The skid-mounted unit, which was leased from Engelhard Industries, was equipped with a blower, preheater, mass flowmeter, catalytic reactor, and temperature controls. A schematic diagram of the catalytic incineration unit is shown in Figure 3. Gases from the solvent generation system were metered into the unit at flowrates ranging from 2.0 to 10 scfm.* Prior to entering the catalyst bed, the gases were heated to the desired temperature with a controlled electric preheater. The electric preheater consisted of a pipe or tube wrapped with an electrical resistance heater element. Test compounds were oxidized on the catalyst bed, and the exhaust was vented. Heat loss from the catalyst bed was minimized by a second electric heater controlling the temperature of the catalyst shell.

Catalyst beds tested consisted of ceramic honeycombs coated with precious metal (platinum/palladium) catalyst. The beds were cylindrical in shape with a 1.5 in. diameter and either a 6 or 12 in. length. Space velocities tested with the catalysts ranged from 15,000 to 80,000 hr^{-1}, and catalyst inlet temperatures tested ranged from 500 to 800°F.

Spiked air streams for testing were generated by evaporating liquid organic compounds into a clean air stream at a controlled rate. Gas samples were withdrawn from the incinerator at three locations: the inlet of the incinerator, the outlet of the electric preheater, and the outlet of the catalyst bed. Concentrations of VOC's present in these samples were determined by two independent methods. Individual compound concentrations were determined by gas chromatography and flame ionization detection (GC/FID, EPA Method 18). Calibration gas mixtures for the GC/FID analysis were prepared dynamically using the same system used in preparing the spiked

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*To convert to metric equivalent, please use the conversion factors listed at the end of this paper.

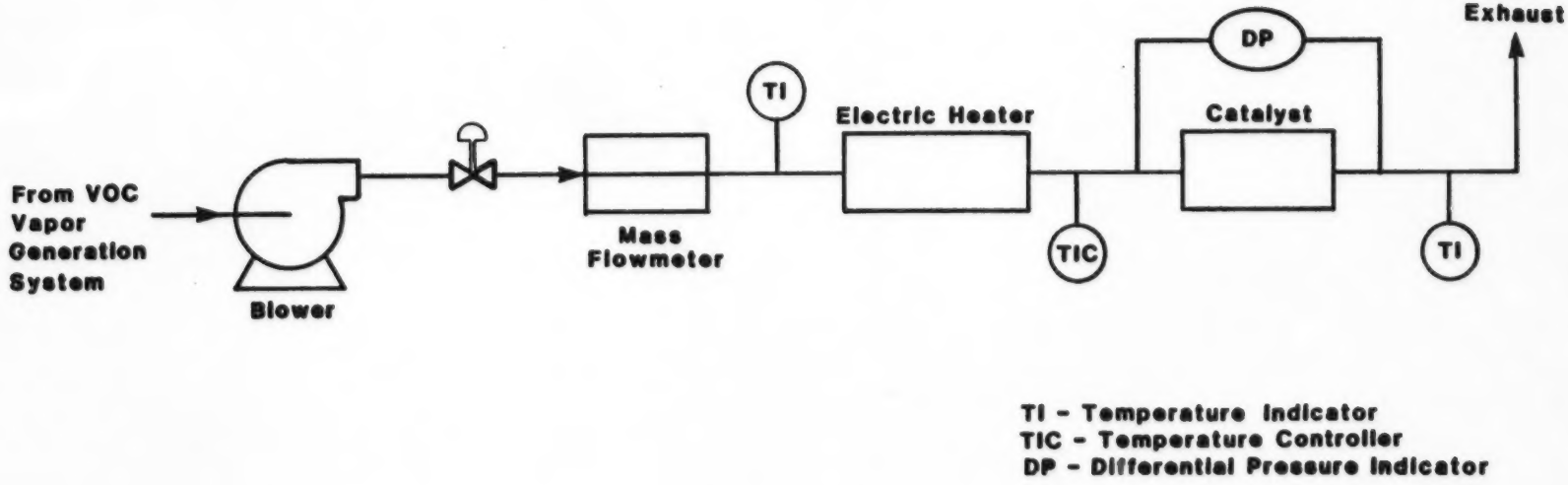

Figure 3. Catalytic Incineration Unit Schematic.

air streams. Total non-methane hydrocarbon (NMHC) concentrations were also determined by flame ionization detection (modified EPA Method 25A). Total NMHC concentrations were quantitated against propane standards.

Experimental Design

Achieving the objective of this study required the selection of a wide range of incinerator operating conditions. Major operating parameters that were varied during the testing included catalyst inlet temperature, compound concentration, space velocity, compound type, catalyst geometry, and catalyst volume. Much of the testing was conducted to characterize compound destruction across the heater and catalyst bed as a "system." However, heater and catalyst destruction efficiencies were also measured separately at a large number of conditions. Test parameters and the range of conditions tested are shown in Table 1.

A total of eight multicomponent mixtures with between two and seven compounds each were tested. In addition, 16 of the compounds were tested singly. Compounds in each of the mixtures are shown in Table 2. Mixtures 1, 1A, 1B, and 1C were used to investigate the effect of combining several compound classes. Mixture 2 represents a typical industrial solvent emission. Mixtures 3, 4, 5 and 6 combined several compounds from one or two classes and Mixtures 7 and 8 were selected to represent hazardous air pollutant (HAP) emissions.

RESULTS

Results from the study provide data showing the effect of incinerator operating conditions and VOC waste gas characteristics on compound specific and overall mixture destruction efficiency. These data are summarized in this section.

Operating Conditions

As expected, compound specific and overall mixture destruction efficiencies were found to be strongly influenced by catalyst inlet

TABLE 1. TEST PARAMETERS AND CONDITIONS FOR VOC/HAP COMPOUNDS

Test Parameter	Conditions or Values Tested
VOC/HAP Mixture	8 multicomponent mixtures and 16 single components[a]
Total Mixture Inlet Concentration (ppmC)[b]	10,000 6,000 1,200
Space Velocity (hr^{-1})[c]	15,000 20,000 30,000 33,000 50,000 80,000
Catalyst Inlet Temperature (°F)	500 680 540 700 580 750 600 800 650
Catalyst Geometry/Volume (ft^3)[d]	Geometry A / 0.006 Geometry A / 0.012 Geometry B / 0.006

[a]Components in the tested mixtures are shown in Table 2.

[b]This is the concentration at the inlet of the electric preheater in parts per million as carbon.

[c]Based on total catalyst volume and gas flowrate at standard conditions (68°F and 14.7 psi).

[d]The larger catalyst volume was achieved by doubling the length of the catalyst while maintaining the same cross-sectional area.

TABLE 2. COMPONENTS IN MULTICOMPONENT VOC/HAP MIXTURES

Mixture 1 - Control Mixture

- iso-Propanol
- Methyl ethyl ketone
- Ethyl acetate
- Benzene
- n-Hexane

Mixture 1A - Hexane Substitution

- iso-Propanol
- Methyl ethyl ketone
- Ethyl acetate
- Benzene
- Cyclohexane

Mixture 1B - Hexane Substitution

- iso-Propanol
- Methyl ethyl ketone
- Ethyl acetate
- Benzene
- iso-Octane

Mixture 1C - Hexane Substitution

- iso-Propanol
- Methyl ethyl ketone
- Ethyl acetate
- Benzene
- n-Octane

Mixture 2 - Industrial Mixture

- Methyl ethyl ketone
- Toluene

Mixture 3 - Alcohols/Acetates

- Methanol
- Ethanol
- iso-Propanol
- n-Butanol
- Ethyl acetate
- n-Propyl acetate
- iso-Butyl acetate

Mixture 4 - Ketones/Miscellaneous Oxygenated Compounds

- Acetone
- Methyl ethyl ketone
- Methyl isobutyl ketone
- Cyclohexane
- Ethyl Cellosolve
- Dioxane

Mixture 5 - Aldehydes

- Propionaldehyde
- iso-Butyl aldehyde
- iso-Valeraldehyde
- n-Butyl aldehyde
- n-Valeraldehyde

Mixture 6 - Alkanes/Aromatics

- n-Hexane
- n-Octane
- n-Decane
- Benzene
- Toluene
- m-Xylene
- iso-Propyl benzene

Mixture 7 - Non-Chlorinated HAP's

- m-Cresol
- Acrylonitrile

Mixture 8 - Chlorinated HAP's

- Methylene chloride
- Carbon tetrachloride
- Ethylene dichloride
- Trichloroethylene
- Tetrachloroethylene
- 1,1-Dichloroethane
- 1,1,2-Trichloroethane

temperature and space velocity. Figures 4 and 5 illustrate the effect of these two parameters on the destruction efficiency of selected mixtures. The data in Figures 4 and 5 show that the destruction efficiency of some mixtures are more strongly influenced by inlet temperature and/or space velocity than others.

For the particular catalytic unit tested under this study, compound destruction in the gas preheater often contributed significantly to the overall "system" (i.e., catalyst plus preheater) destruction efficiency. Relative contributions of preheater and catalyst destruction efficiencies for Mixture 1 are shown in Figure 6. The degree to which heater destruction efficiencies observed during this study may represent heater or burner zone destruction efficiencies on full-scale catalytic incinerators is not known. Most full-scale incinerators requiring waste gas preheat employ natural gas preheaters instead of electrical resistance heaters. Compound destruction in these natural gas preheaters may vary considerably depending on the preheater design.

Other test results relating to incinerator operating conditions showed the importance of catalyst geometry and catalyst volume. For one test series, catalyst surface area was increased by reducing the honeycomb cell size, and in another test series, the catalyst volume was increased by doubling the catalyst length. Both the increased surface area and the increased volume resulted in improved destruction efficiency, with the greatest improvement occurring at low temperatures and high space velocities.

VOC Composition/Concentration

The effect of VOC concentration was evaluated by testing Mixture 1 and the single compounds in Mixture 1 at total concentrations of 1,200 and 6,000 ppmv. The results indicated that higher concentrations did result in slightly higher compound destruction efficiencies. This effect was more evident at low temperatures (580°F) than at high temperatures (750°F).

The effect of compound class was determined by comparing the destruction efficiencies of various compounds and compound classes at given combinations of temperature, space velocity, and VOC concentration. This comparison provided the following ranking of compound classes:

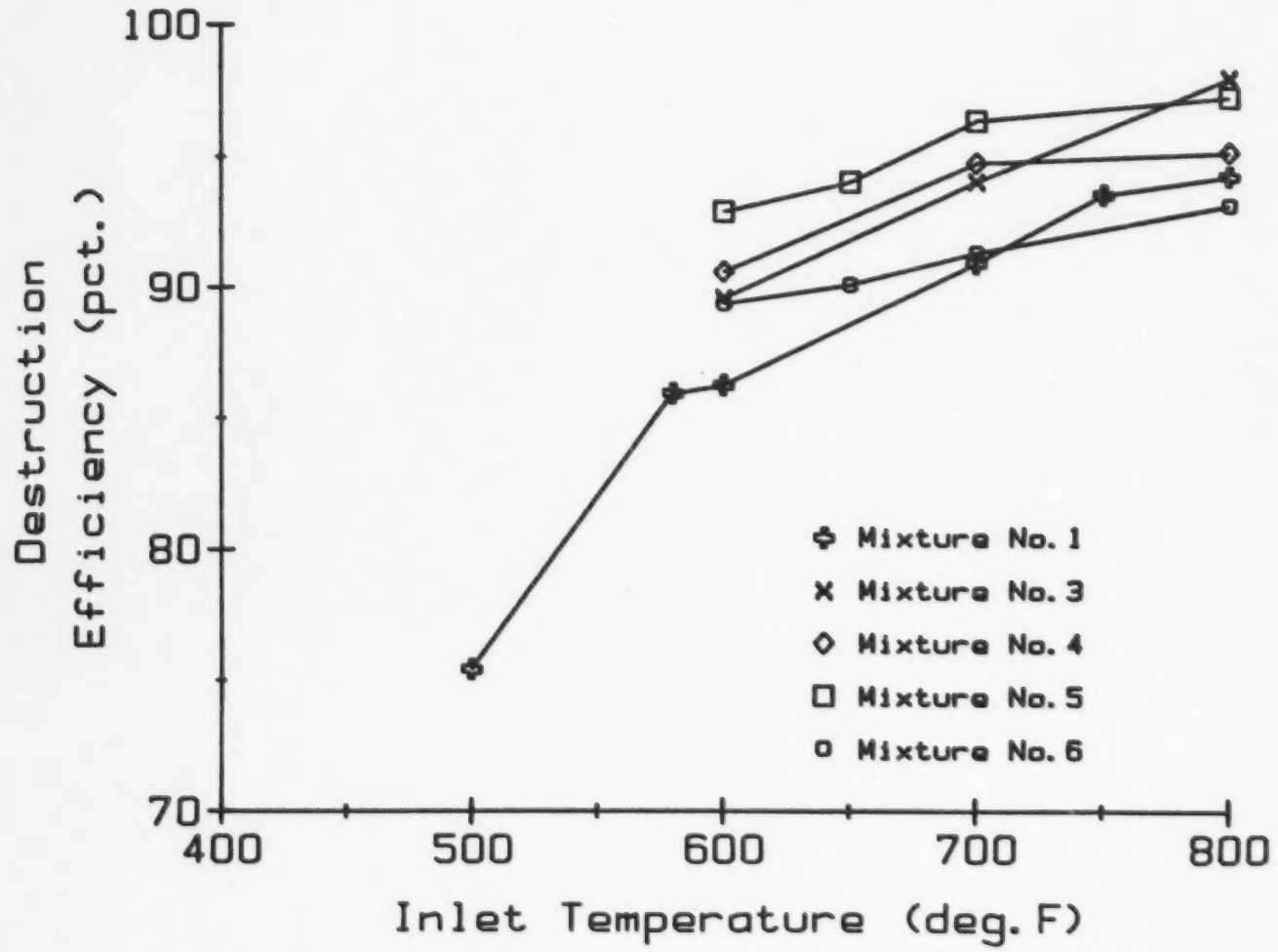

Figure 4. Effect of Temperature on Destruction Efficiency
(Space Velocity = 50,000/hr)

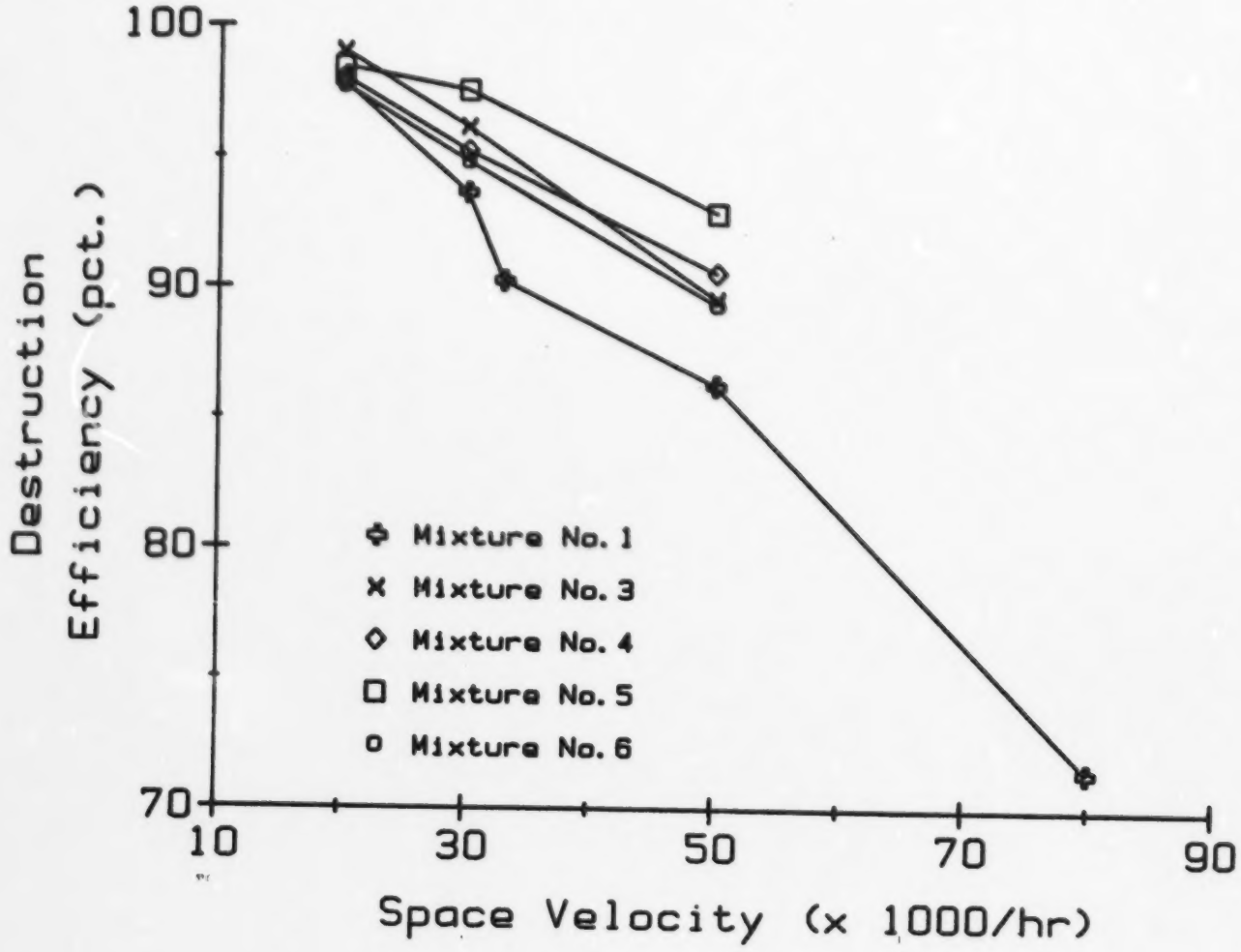

Figure 5. Effect of Space Velocity on Destruction Efficiency (Temperature = 600°F)

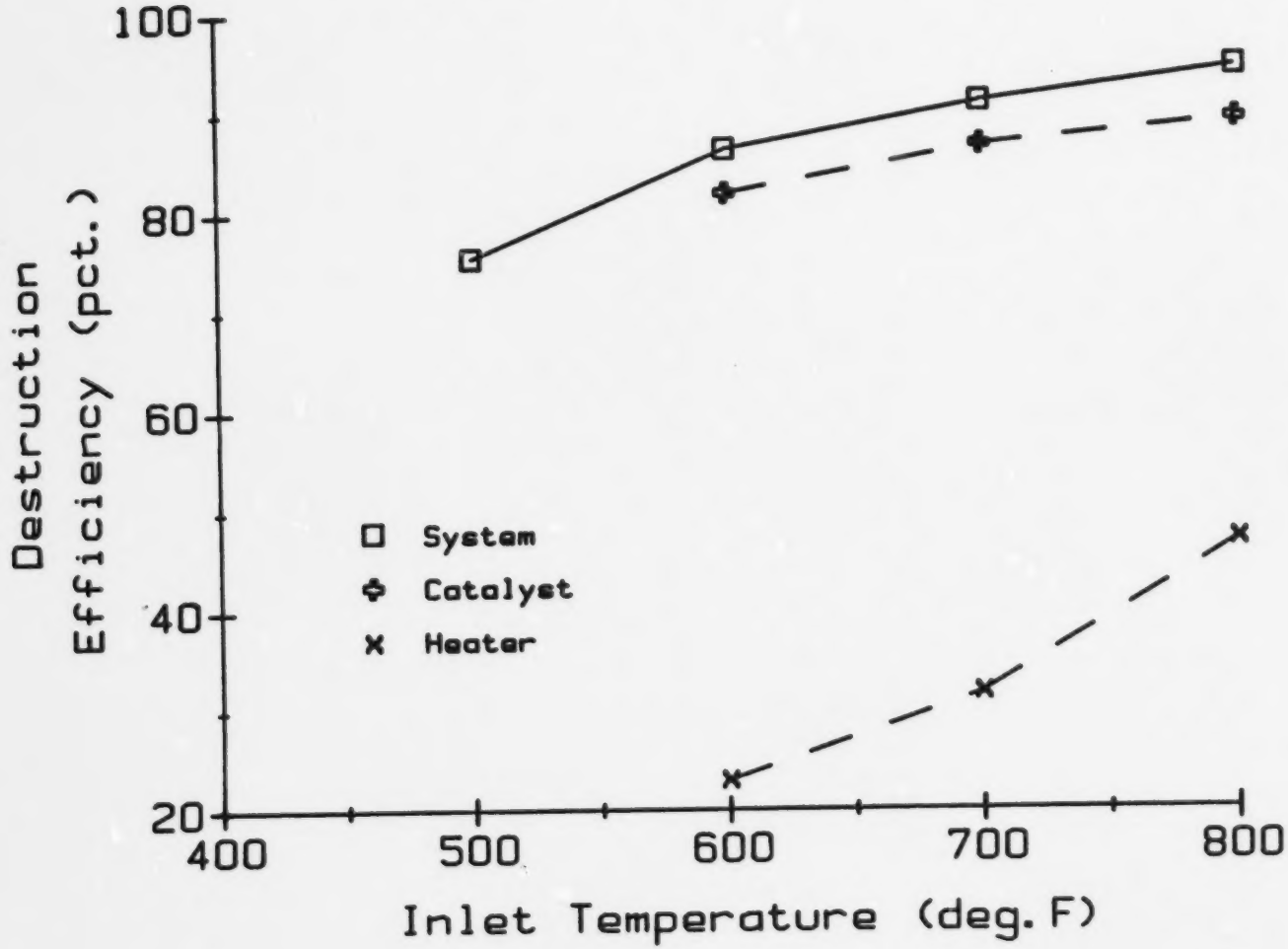

Figure 6. Relative Contribution of Heater and Catalyst to System Destruction Efficiency (Mixture No. 1; Space Velocity = 50,000/hr)

Compound Class	Relative Destructibility
Alcohols	High
Cellosolves/dioxane	
Aldehydes	
Aromatics	
Ketones	
Acetates	
Alkanes	
Chlorinated hydrocarbons	Low

All of the compound classes, except chlorinated hydrocarbons, were able to be destroyed with 98 - 99% efficiency at sufficiently low space velocities/ high temperature. A destruction efficiency of 97% was achieved for acrylonitrile and cresol (Mixture 7). It should be noted that the ranking provided above is generally applicable to classes of compounds; specific compounds within each class may exhibit different relative destructibilities when compared to other compounds within the same or different classes.

The destruction efficiency for the chlorinated hydrocarbons was quite low. In addition, tests conducted after the chlorinated hydrocarbon "burns" showed that the catalyst had been partially deactivated.

The effect of compound mixtures is best illustrated by comparing the destruction efficiencies of specific compounds when tested alone vs. their destruction when tested in mixtures. If the "mixture effect" were negligible, these efficiencies would be similar. Figure 7 shows the results of tests conducted on single compounds at 1200 ppmv. Note that significant differences exist between the individual destruction efficiencies. Figure 8 shows the results of testing these same compounds (except iso-octane) in a mixture at 1200 ppmv. As in the single compound tests (Figure 7), there are obvious differences between the destruction efficiencies for the individual compounds. It is noted, however, that the compound destruction for some of the compounds is quite different when Figures 7 (single compounds) and 8 (mixture) are compared. For example, hexane achieved greater than 90%

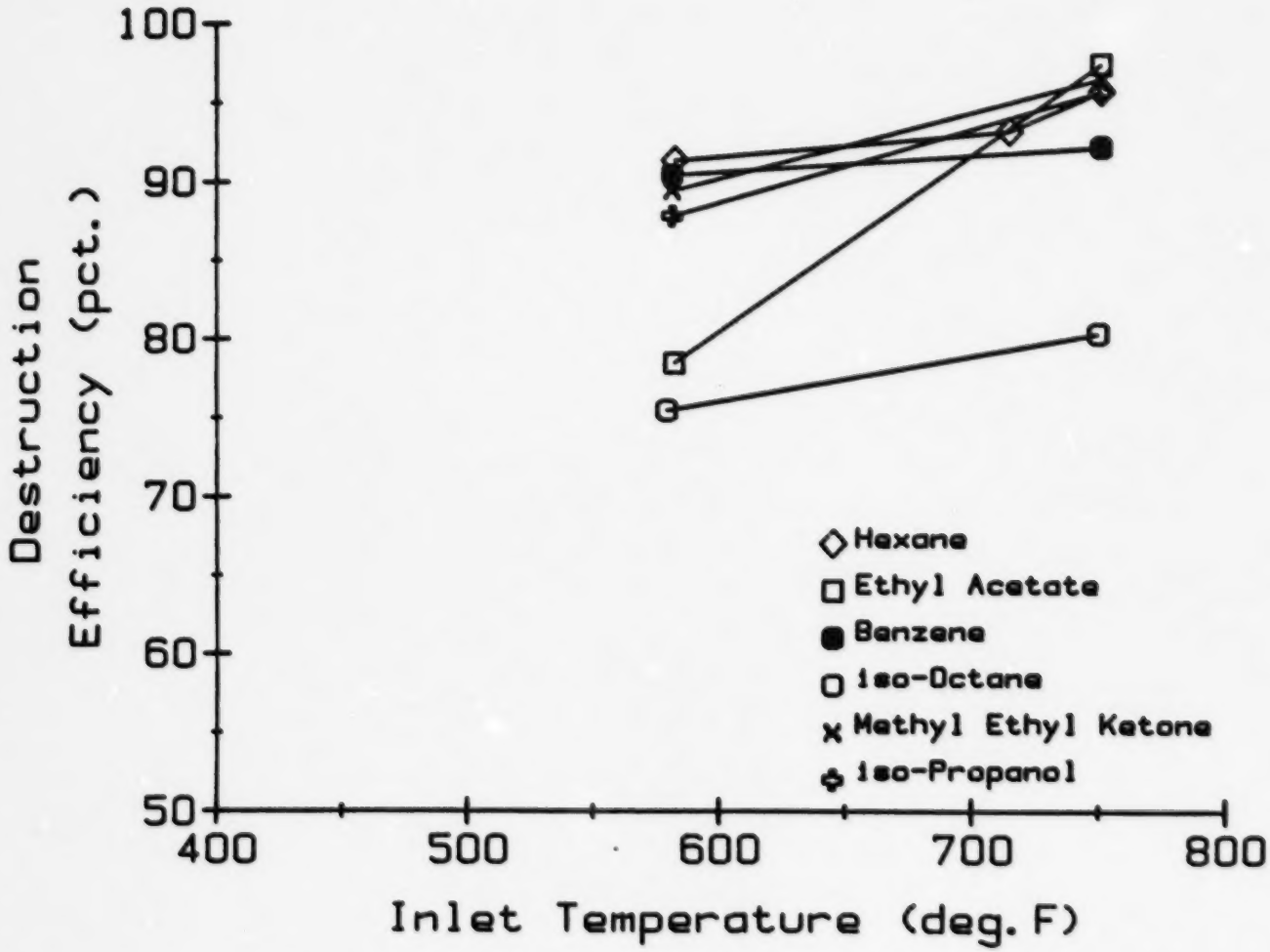

Figure 7. Destruction Efficiency for Single Compounds vs. Temperature (Space Velocity = 50,000/hr)

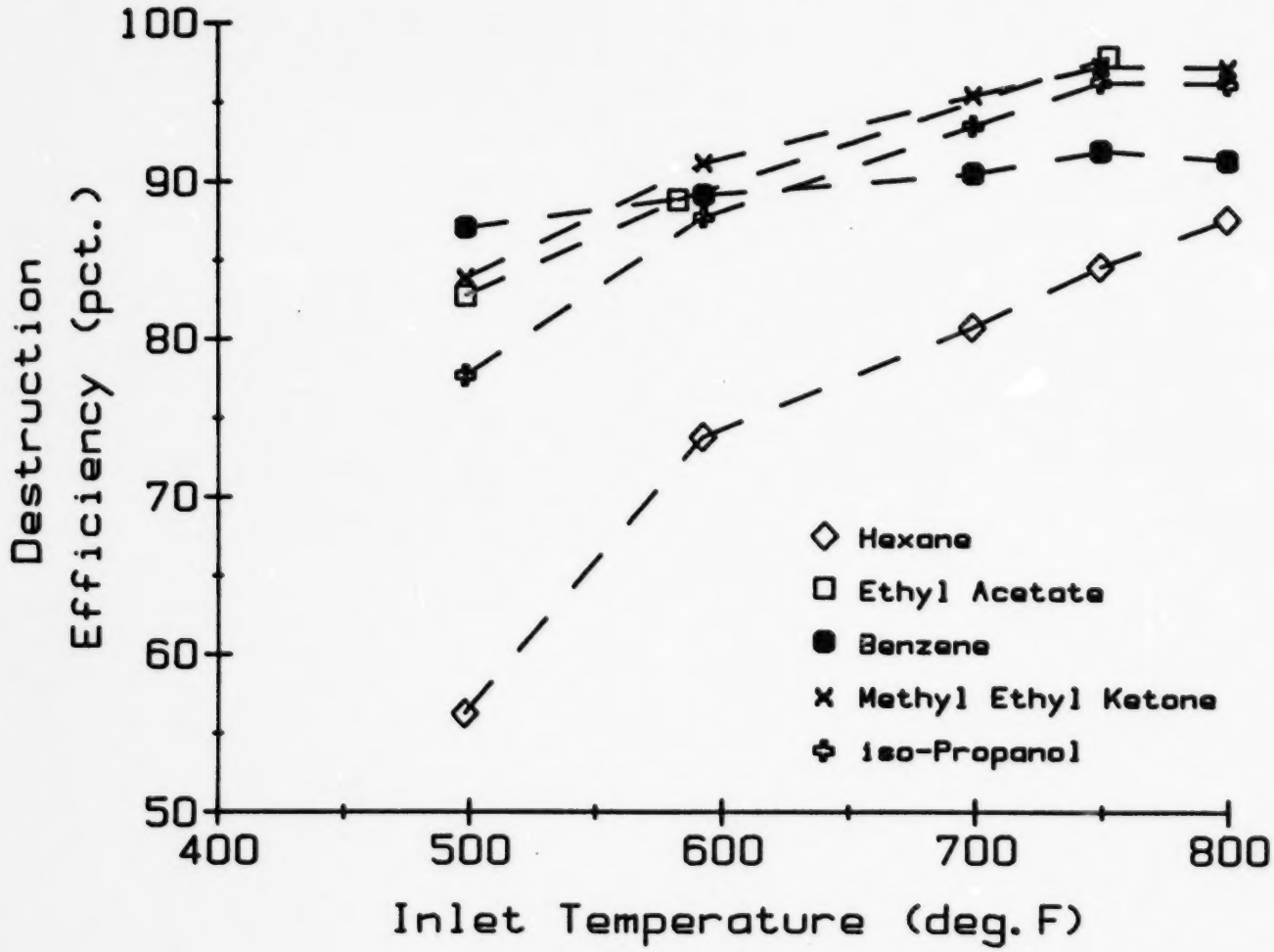

Figure 8. Destruction Efficiency for Compounds in Mixture No. 1 vs. Temperature (Space Velocity = 50,000/hr)

destruction at 580°F when incinerated alone (Figure 7), but was less than 75% destroyed at the same temperature when combusted in a mixture (Figure 8). This effect is further illustrated in Figure 9, which clearly shows that hexane is more effectively destroyed when incinerated by itself. Figure 9 also shows that the type of mixture has an effect; note that the efficiency reduction is much less for Mixture 6 (alkanes and aromatics) than for Mixture 1 (five compound classes). The "mixture effect" is not consistent between compounds. Figure 10 shows that the destruction of ethyl acetate was greater when burned in a mixture than by itself. Finally, some compounds showed no effect; benzene, for example, showed no differences in destruction efficiencies due to mixture (see Figure 11).

CONCLUSIONS

The following conclusions are based on the results discussed above. While some may be applicable to catalytic incineration of VOC's in general, they are presented here as applying only to the test catalyst and ranges of conditions tested:

(1) VOC compound destruction efficiency increases with increasing temperature and decreasing space velocity.

(2) VOC compound destruction efficiency increases with increasing concentration.

(3) The destructibility of VOC's varies according to compound class.

(4) Individual VOC's have different destruction efficiencies (at a given concentration, temperature, and space velocity).

(5) Different destruction efficiencies may be obtained for a specific VOC incinerated in a mixture vs. when burned alone.

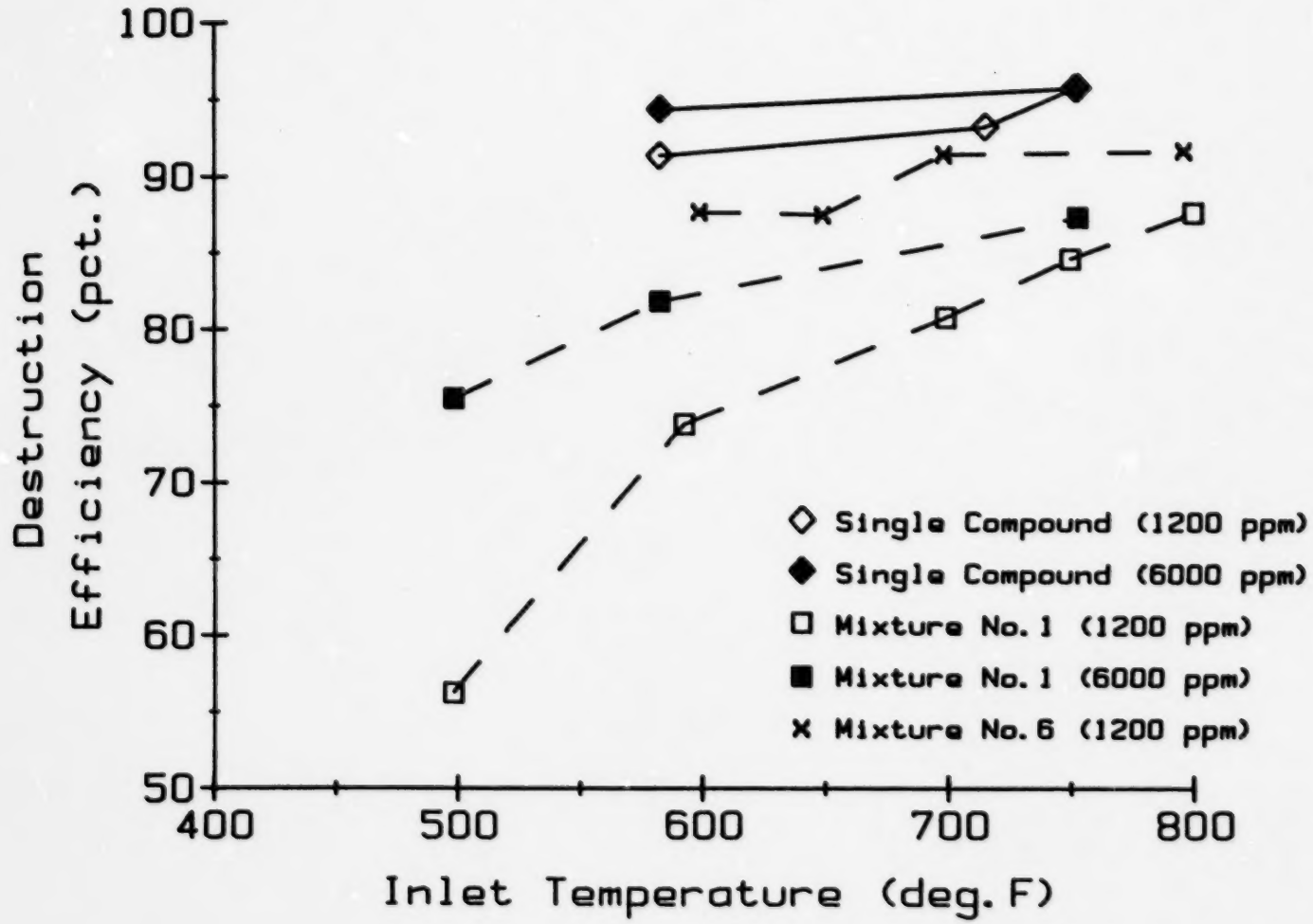

Figure 9. Destruction Efficiency for n-Hexane vs. Temperature
(Space Velocity = 50,000/hr)

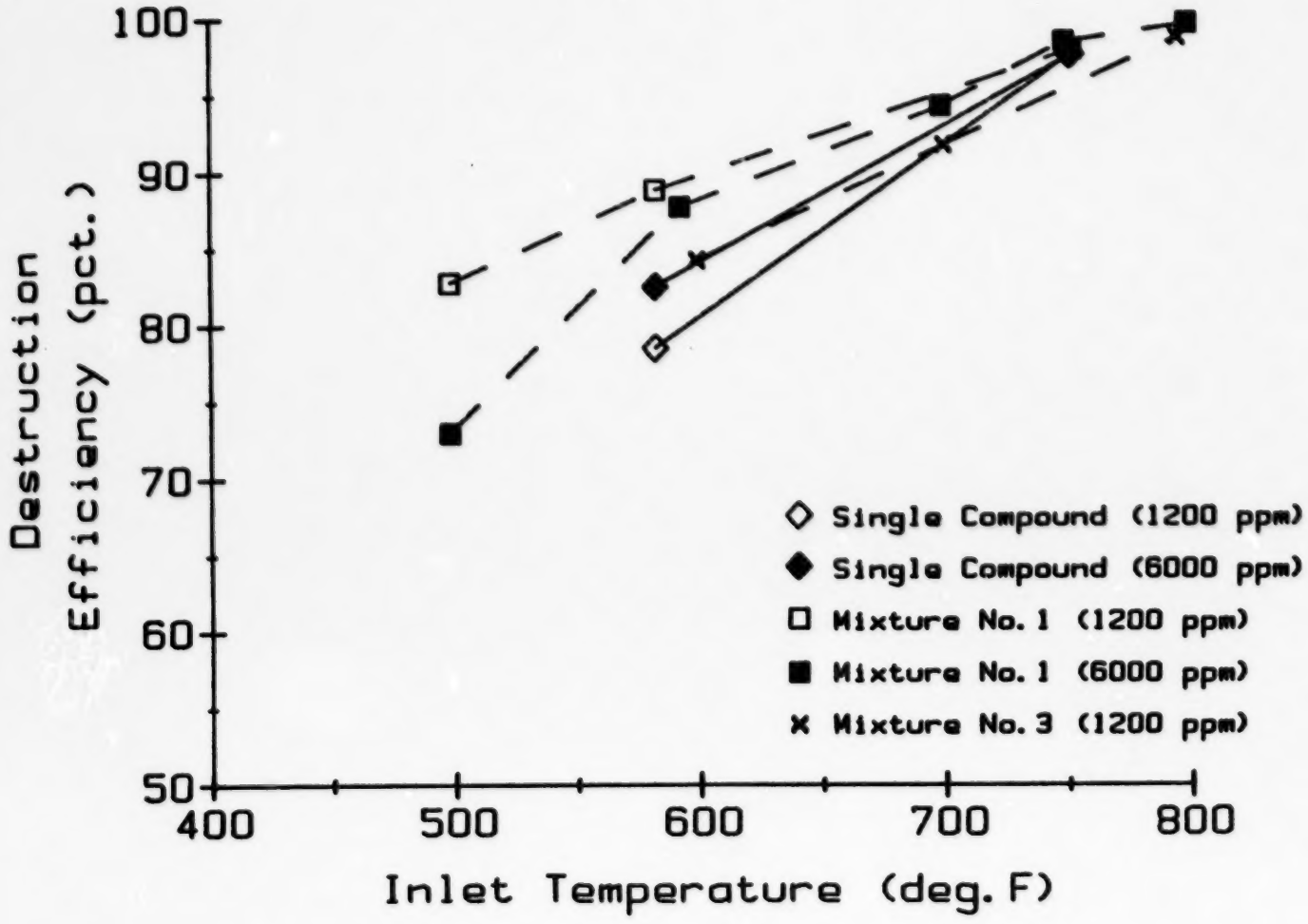

Figure 10. Destruction Efficiency for Ethyl Acetate vs. Temperature (Space Velocity = 50,000/hr)

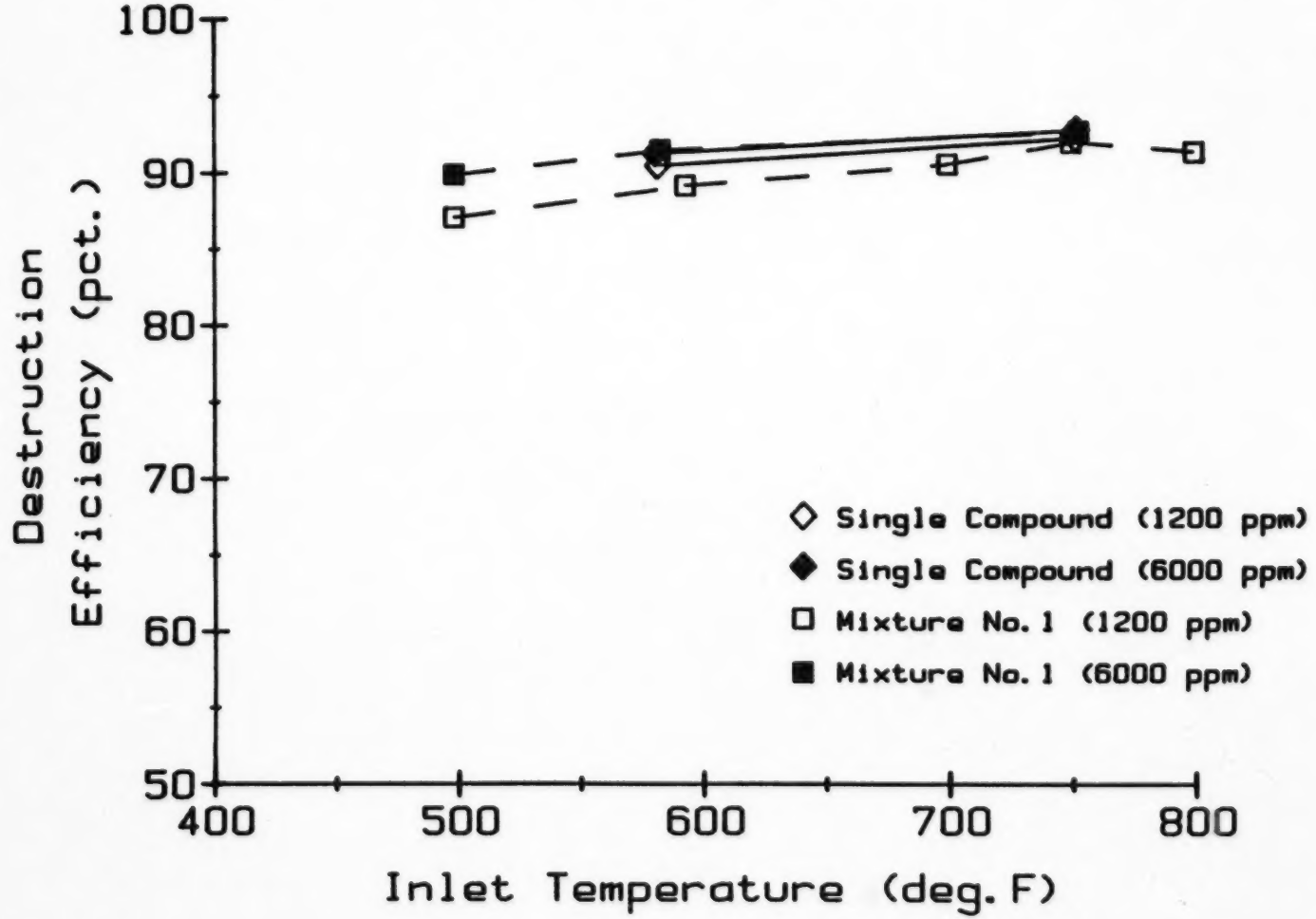

Figure 11. Destruction Efficiency for Benzene vs. Temperature
(Space Velocity = 50,000/hr)

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CONVERSION FACTORS

To convert nonmetric units used in this paper to their metric equivalents, please use the following factors:

Nonmetric	Multiplied By	Yields Metric
cfm	1.699	m^3/h
ft^3	0.02832	m^3
in.	0.0254	m
psi	6895	Pa

°F is converted to °C via: °C = 5/9 (°F - 32)